

SMX 3161.2 (98-13DIV2)
PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of Shenheng Guan et al.

Art Unit 1743

Serial No. 10/071,546

Filed February 8, 2002

Confirmation No. 9873

For APPARATUS FOR SCREENING CATALYSTS IN A PARALLEL FIXED-BED
REACTOR

Examiner Dwayne K. Handy

DECLARATION OF PRIOR INVENTION UNDER 37 CFR § 1.131

I, Shenheng Guan, declare as follows:

1. I am currently an associate adjunct professor in the Department of Pharmaceutical Chemistry at the University of California, San Francisco.
2. From October, 1996 to January, 2002, I was employed as a Distinguished Scientist at Symyx Technologies, Inc. (Santa Clara, California), the assignee of the above-referenced U.S. patent application, Serial No. 10/071,546.
3. I am named as a joint inventor in the above-referenced patent application and I am the sole inventor of some of the claimed subject matter, including the invention defined in independent claims 61-63 and dependent claims 70 and 80-87 depending therefrom as currently amended and presented in Amendment C.
4. I conceived of and, with the assistance of other Symyx employees, reduced to practice in the United States the subject matter of the invention as defined in currently amended independent claims 61-63 and dependent claims 70 and 80-87 depending therefrom before February 19, 1998, the facts being set forth below.
5. The invention described and claimed in the subject patent application was developed as part of a materials research program that I participated in while employed at Symyx Technologies, Inc.

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6. Exhibit A, attached to this Declaration, is a true and correct copy of an internal research report I prepared prior to February 19, 1998 in connection with the above-mentioned research program as part of my duties at Symyx Technologies, Inc. The report describes the conception and development of a parallel fixed-bed reactor for screening catalysts and evinces my conception of the subject matter of currently amended independent claims 61-63 and dependent claims 70 and 80-87 depending therefrom and reduction to practice of an operational "six-channel prototype reactor" prior to February 19, 1998.

7. Exhibit B, attached to this Declaration, is a true and accurate copy of laboratory notebook pages I prepared prior to February 19, 1998 in accordance with established practices while employed at Symyx Technology, Inc. These notebook pages were prepared and include data recorded in connection with screening samples of molybdenum-vanadium-niobium oxide (Mo-V-Nb-O) catalysts in the gas-phase dehydrogenation of ethane to ethylene using the above-referenced parallel fixed-bed reactor. In particular, on pages 86-89 of the notebook, I carried out a number of experimental runs using the six-channel parallel fixed-bed reactor and catalysts of varying composition. In these experiments, reaction vessels 1-3 contained a sample of a particular catalyst (designated in the notebook as CX 1023 through CX 1029) and reaction vessels 4-6 contained a sample of a catalyst of different composition (designated in the notebook as CX 2023 through CX 2029). The composition of the gaseous effluents exiting the reaction vessels were measured using two gas chromatographs (GCs) containing three identical GC channels. The reactions were carried out at approximately atmospheric pressure and the temperature was controlled at about 300°C. The actual temperature measured in the reaction vessels is recorded in the notebook pages along with the GC peak area readings for CO, CO₂, and C₂H₄ measured in the respective gaseous effluents exiting the six-channel parallel fixed-bed reactor during dehydrogenation of ethane to ethylene. The data recorded in these notebook pages was used to determine the conversion and selectivity obtained using the different catalysts.

8. The data recorded in the notebook pages of Exhibit B are in part the basis for my statement in Exhibit A that "Currently, the six-channel prototype reactor is operational and producing reliable data."

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9. All work referred to herein was carried out in the United States.

10. All statements that I made herein of my own knowledge are true and all statements made on information and belief are believed to be true. I acknowledge that willfully making false statements is punishable by fine, imprisonment, or both, under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of any patent issuing from this application.

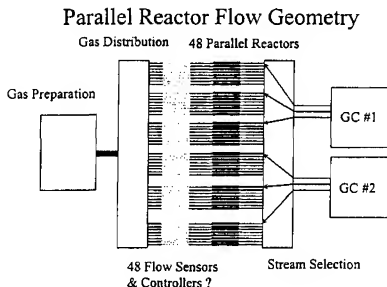

Shenheng Guan

9/28/06
Date

Symyx Parallel Fixed Bed Reactor

Shenheng Guan

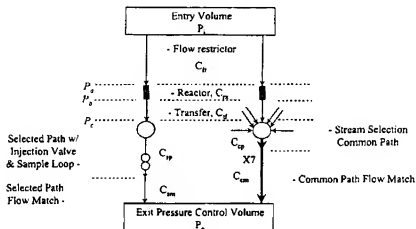
The Design philosophy of the parallel fixed bed reactor is to scale down from conventional laboratory reactors and to operate many reactors simultaneously. By choosing catalyst loading to be two orders of magnitude lower than that in conventional reactors, many catalysts can be synthesized quickly. Since many important parameters, such as space velocity, contact time, and power forms of catalyst, can be preserved, data from the reactor can often be compared with that from conventional methods directly. Final version of the parallel reactor contains 48 individual reactors.



Design of the parallel fixed bed reactor offers several advantages over single bed reactors. It allows creation of nearly identical reaction conditions for all the individual reactors and allows one to carry out catalyst activation and catalytic reactions simultaneously. With a careful design, reaction conditions for the individual reactors can be controlled – creating opportunities for combinatory studies of reaction conditions for the same catalyst. Six identical gas chromatography (GC) channels analyze products simultaneously. Since 48 reactors need to be analyzed, sophisticated gas distribution and stream selection valve control methods are introduced. By use of GC for detection, almost all possible reaction systems can be investigated. The parallelism of the reactor allows analysis process to be pipelined, therefore, characterization time can be minimized.

The key design concept of the reactor is to use flow restriction upstream from individual reactors. By supplying a common inlet pressure and a common outlet pressure, the flow rate of the individual reactor is determined mainly by conductance of the flow restriction.

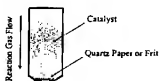
Parallel Reactor Flow Matching



If the flow restriction has conductance orders of magnitude smaller than that of the rest flow path and all reactors have the same flow restriction, the variation of conductance among reactors (for example, by catalyst packing) will not cause large variation in flow rate. Mass flow controllers premix reaction gas that is then supplied to all the reactors through a bundle of long and narrow bore capillaries (as flow restrictors). Flow measurement has been done on the six-channel prototype reactor. A flow variation of less than 2% was observed.

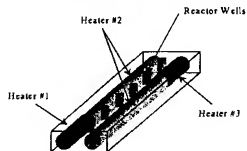
The prototype reactor block was constructed with stainless steel. Catalysts are contained in cartridges made of quartz or stainless steel.

Parallel Reactor Catalyst Cartridge



Quartz paper is used as frit to prevent power from escaping from the cartridge. The reaction block can be opened on the top to expose all the catalyst cartridges, allowing easy sample change. A three heating zone method is developed to achieve uniform temperature distribution among reactor wells.

Temperature Control Method in Parallel Reactor



The three zones are independently controlled with PID loops. A temperature spatial variation below 4°C at 350°C has been realized. The additional benefit from such method is a linear temperature gradient can be easily generated. A 10°C difference between adjacent reactors was obtained. Currently, the six-channel prototype reactor is operational and producing reliable data.

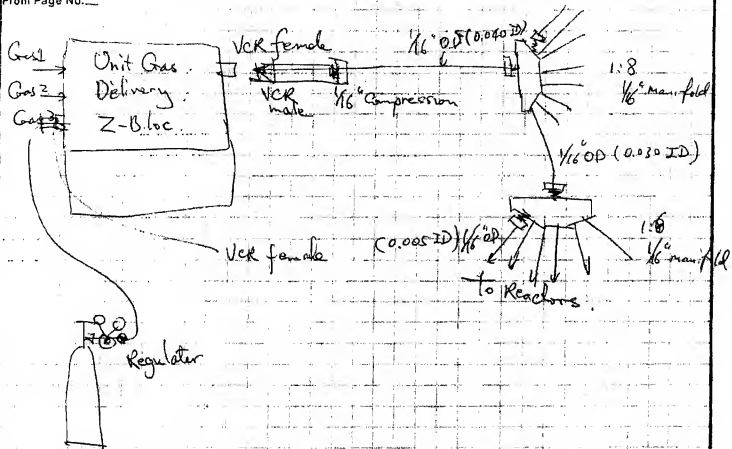
Micro Fiched

On _____

NOTEBOOK NO. L (23)
ISSUED TO SILVERMONT C. M.
ON 10/14 19 96
DEPARTMENT Analytical Technology
RETURNED 19

—SCIENTIFIC NOTEBOOK CO.—
2831 LAWRENCE AVE.
P.O. BOX 238
STEVENSVILLE, MI 49127
616-429-8285

From Page No. _____



Regulator :

 $\frac{1}{4}$ " NPT to $\frac{1}{4}$ " Compression

X 3

5-10 w. $\frac{1}{4}$ " OD line

X 3

 $\frac{1}{4}$ " Compression to $\frac{1}{4}$ " VCR female

X 3

VCR male to $\frac{1}{16}$ " Compression

X 1

 $\frac{1}{16}$ " to $\frac{1}{4}$ " Reducer

SS-4-VCR-6-400

SS-4-VCR-P

CU-4-VCR-2

SS-400-R-4

To Page No. _____

Witnessed & Understood by me,

RMA made

Date

Invented by

Recorded by

[Signature]

STEVEN H. GUAN

Date

|||

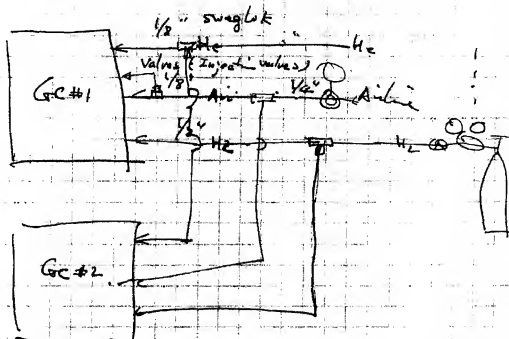
Project No. _____

TITLE _____

Book No. _____

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From Page No. 44



To Page No. _____

Witnessed & Understood by me,

R. R. R. R.

Date

Invented by

[Signature]

Date

Recorded by

STEWART G. GUN

Project No. _____

Book No. _____

TITLE

tested Milestone on Para Reactor

From Page No. _____

Flow : CH₁ 37.5% 3.75 sccm 14.4% O₂ in N₂
 CH₂ 3.0% 2.50 sccm Ethane

P₁ = 8 psigP₂ = 7 psigP₃ = 0 psig

start 9:30 am

Temperature :

1	2	3	4	5	6	7
262.1	280.3	281.1	279.3	274.2	262.0	

File CX-1023

Bad

CX-2023

Good

	CO	CO ₂	C ₂ H ₄	Temp
1	0.0689	0.0718	0.1408	262.1
2	0.0850	0.0870	0.1691	280.3
3	0.0856	0.0759	0.1747	281.1
4	0.244	0.1747	2.9458	279.3
5	0.2394	0.1713	3.080	274.2
6	0.1427	0.0992	2.232	262.0

To Page No. _____

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RMM/male

Date

Invented by

Recorded by

hjh

SHI ZHONG

Date

||||

TITLE _____

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Book No. _____

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From Page No. ⁸⁶

Film	EX1024	EX2024	Rad Cross	
	CO	CO ₂	CH ₄	Temp
1	0.0677	0.0688	0.1563	265.1
2	0.0814	0.0718	0.1844	280.5
3	0.0847	0.0655	0.1924	280.2
4	0.2727	0.2090	3.1700	280.0
5	0.2703	0.2057	3.325	276.1
6	0.1685	0.1257	2.513	265.2

Temp 280 → 300 EX1025
EX1025

1	0.1126	0.0939	0.2689	284.1
2	0.1331	0.1051	0.3150	300.9
3	0.1369	0.0967	0.3295	301.3
4	0.6164	0.5112	4.9116	300.0
5	0.6398	0.4812	5.1608	294.3
6	0.4157	0.3202	4.0752	284.1

To Page No. _____

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R. M. M. M.

Date

Invented by

[Signature]

Date

Recorded by

SHEN HENG

From Page No. ⁸⁸2

1:22 pm

300°C → 350°C

Cx 7028
Cx 2028

CO₂ CO₂ C₂H₄

Temp

1	0.2896	0.4040	0.8832	333.9
2	0.3587	0.4586	1.0216	350.9
3	0.3961	0.4077	1.0775	351.5 353.5
4	0.4481	1.9014	9.3465	350.1
5	2.7859	1.8087	17.134	345.1
6	2.244	1.633	9.0623	334.8

300°C → 350°C

Cx 11029
Cx 1029

1	0.1151	0.1257	0.3904	300.1
2				
3				
4				
5				
6	0.7949	0.1813	5.731	300.3

To Page No. _____

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RMBBmk

Date

Invented by

hlg

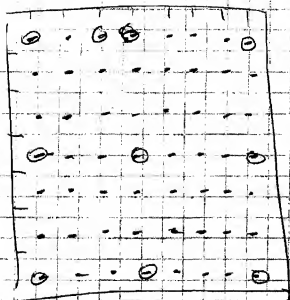
Date

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SHENHENG GOAN

From Page No. _____

28 Reader thermocouple distribution



To Page No. _____

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R. H. H. H. H.

Date

Invented by

R. H. H. H. H.

Date

Recorded by

J. H. H. H. H.

From Page No. _____

Diapling's Cat

CX1001
CX2002

Catalyst
preparation

12x Temp Temp (Treated)

Not compressed

1

282.7 400 4h

2

301.0 400 8h

3

301.2 400 12h

Compressed

4

300.0 400 4h

5

295.2 400 8h

6

284.7 400 12h

Flow changed to

Ch 1 75.0%

7.5 secm 14.9% O₂ in N₂

Ch 2 10.0%

5.0 secm Ethane

P1: 1.2 psig

P2: 1.2 psig

P3: 0

CX1002
CX2002

To Page No. _____

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RMA/Bonal

Date

Invented by

[Signature]

Date

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SUZUENGA GUAN

From Page No. _____

Top Blacknet Bolted Down

Temperature Setting 2000°C D Ch 4 for 30 mins

1	2	3	4	5	6
188.3	202.4	201.5	200.3	196.7	188.0

Temperature Setting 3000°C D Ch 4 for 1 hour

1	2	3	4	5	6
282.8	302.5	301.5	300.0	295.4	283.8

Dam's Cat 102-11-B / ^{105ccm} ch flow 18.7% ^{505ccm} Ethane

Cat loading (mg) ¹ 53.4 ² 52.3 ³ 56.7 ⁴ 53.8 ⁵ 50.4 ⁶ 32.2 ⁷ 20.0

CX1004 2005

CX1005 2006 235.6 251.8 251.8 250.0 245.7 236.4 250°C

CX1007 2008 282.9 302.0 301.8 300.2 295.1 286.3 300°C

CX1008 2009 309.7 352.1 351.9 349.8 343.6 330.1 350°C

CX1009 2010 378.7 402.3 402.4 400.4 394.1 377.7 400°C

CX1010 2011 429.5 453.4 453.7 451.8 445.7 428.9 450°C



To Page No. _____

Witnessed & Understood by me,

RBSBonde

Date

Invented by

RBSBonde

Date

Recorded by

S. R.

|||

TITLE _____

Project No. _____

Book No. _____

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From Page No. _____

Compensated Heating System control for main heaters

1 2 3 4 5 6

Parallel React
PR DATA/
12-31-97-1

10:01:53

209.2, 203, 200, 199 200 200.2

CX1001 CX2001

10:27:17

249.0 255 251 249 250 249.5

CX1002 CX1002

10:51:09

298.0 305 301 299 299 299.5

CX1003 CX2003

11:31:09

349.9 356 350 349 349 350.0

CX1004 CX2004

11:56:25

395.4 405 400 398 399 399.8

CX1005 CX2005

12:00:36

447.2 455 450 448 449 449.8

CX1006 CX2006

~~304.0 344 350 357 267 370.0~~
320 340 370 607

14:01:36

317.7 336 342 349 359 367.9

07

14:09:44

319.5 336 340 347 358 361.2

08

14:27:21

319.8 336 350 347 359 369.8

09

To Page No. _____

Witnessed & Understood by me,

Date

Invented by

Date

RH. Borden

Recorded by

S. Gm

Project No. _____

Book No. _____

TITLE PR Calibration #2

From Page No. _____

Matheson Certified Gas STD 6 Component (MR1543)

	Prep.	Actual
CO	22%	1.97%
CO ₂	22%	1.97%
O ₂	40%	3.89%
Ethylene	60%	6.06%
Ethane	30%	30.10%
B ₂	—	Balance

Calibration gas 2 at 1 to 30% ~ 3 scfm

11 runs collected

Data on Enigma / Storage / Parallel Reader / PR Data
11-2-98-1CX1006 - CX1010 } used for calibration
CX2006 - CX2010

To Page No. _____

Witnessed & Understood by me,

RABonde

Date

Invented by

Recorded by

Date